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Computational Molecular Modeling of the Multi-Scale Dynamics of Water and Ions at Cement Interfaces

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Abstract Structural and dynamic behavior of H_2O molecules and aqueous at interfaces and in nanopores of model C-S-H binding phase (tobermorite) is quantified on the basis of molecular dynamics computer simulations. At the (001) surface of tobermorite in contact with 0.25 M KCl aqueous solution, we can effectively distinguish water molecules that spend most of their time within channels between the drierketten chains of silica on the tobermorite surface from the adsorbed molecules residing slightly above the interface. Within the channels, H_2O molecules donate H-bonds to both the bridging and non-bridging oxygens of the Si-tetrahedra as well as to other H_2O. Some of these molecules form very strong H-bonds persisting over 100 ps and longer, but many others undergo frequent librations and occasional diffusional jumps from one surface site to another. The average diffusion coefficients of the surface-associated H_2O molecules that spend most of their time in the channels and those that lie above the nominal interface differ by about an order of magnitude (D_{H2O}[internal]=5.0×10^{-11} m^2/s and D_{H2O}[external]=6.0×10^{-10} m^2/s, respectively). The average diffusion coefficient for all surface-associated H_2O molecules is about 1.0×10^{-10} m^2/s. All of these values are significantly less than the value of 2.3×10^{-9} m^2/s, characteristic of H_2O self-diffusion in bulk liquid water, but they are in very good quantitative agreement with experimental data on the dynamics surface-associated water in similar cement materials obtained be ^1H NMR [1,2].

Introduction

To better understand and reliably predict long-term properties of the nuclear waste packages and cement barriers, it is crucial to develop quantitative approaches to understanding the cement hydration behavior and the properties of hydrated paste on a fundamental molecular scale. At solid surfaces of cement phases and in their nanopores, individual water molecules and hydrated ions simultaneously participate in several dynamic processes, which are characterized by

different, but equally important time- and length- scales. On a relatively long time scale (~100-1000 ps), we are able to quantify the diffusional processes related to reformation of the entire interfacial H-bonding network, surface adsorption of H_2O molecules, and ions. The interfacial dynamics on the intermediate time scale (~1-10 ps) is dominated by the molecular librational and re-orientational motions. The librations (hindered rotations) of surface hydroxyls also occur at this time scale. These motions are responsible for the reformation and breaking of individual hydrogen bonds, while the strength of these bonds can be directly correlated with the frequencies of intra-molecular O–H vibrations on the shortest, sub-ps time scale. Most of these processes are very difficult to investigate experimentally. They require a broad range of sophisticated analytical techniques, and it is not always possible to interpret their results in a unique and entirely convincing way. Despite decades of study, the structure, dynamics and physical properties of water in cement materials remain incompletely understood [3], although experimental studies involving especially field cycling NMR relaxation and quasielastic and inelastic neutron scattering methods are adding significant new insight in recent years [1-2,4-6].

At the same time, computational molecular modeling approaches are now offering significantly better quantitative atomistic scale picture of water behavior in cement systems [7-14]. Here we present a brief summary of our recent attempts to quantify the structural and dynamic behavior of aqueous solutions at interfaces and in nanopores of cement materials, focusing on the computer simulations of the principal binding phase, known as C-S-H (tobermorite).

Models and Methods

As in our previous simulations [7,10,15], simulated C-S-H model is based on the structure of the 9Å phase of tobermorite, $Ca_5Si_6O_{16}(OH)_2$, determined by Merlino et al. [16] using single crystal X-ray diffraction methods. The simulation supercell had dimensions of $22.63 \times 29.19 \times 58.18$ Å^3 and contained $2 \times 4 \times 2$ crystallographic unit cells of 9Å tobermorite in contact with ~40 Å layer of 0.25 M KCl aqueous solution (Fig.1). This is comparable to the electrolyte concentrations found in the pore solutions of cements [17,18]. Periodic boundary conditions were then applied in all three dimensions to produce models of the interfaces formed by the solid layers interspersed with 4-nm-thick layers of aqueous solutions, thus representing a simple model of a slit-like cement nanopore. On the other hand, the thickness of the solution layer was sufficiently large to effectively exclude direct interactions between two different solution/solid interfaces created due to the periodicity of the system. The number of H_2O molecules in this layer was chosen to reproduce the density of bulk aqueous solution under ambient conditions (~1 g/cm^3).

CLAYFF force field [19] was used to define all interatomic interactions in the model system. This force field has already been successfully applied to

simulate a wide range of minerals and interfaces [20-23], and is known to accurately reproduce the structure of tobermorite [7,10]. Our model assumes a fully polymerized drierkette chain structure, and in order to have the stoichiometric composition of $Ca_5Si_6O_{16}(OH)_2$, one half of the non-bridging oxygens of the Si-tetrahedra (those pointing outward of the surface) were assumed to be Si–O–H, while the other half (those pointing parallel to the surface) we assumed to be non-protonated $Si–O^-$ (Fig. 1). Thus, the model surface was considered electrostatically neutral.

The MD simulations were performed in the statistical *NVT*-ensemble with a time step of 0.001 ps, and the equilibrium MD trajectory of the system was recorded for further statistical analysis every 0.005 ps over a period of 1 ns after a pre-equilibration period of approximately 0.1 ns. This time scale is approximately an order of magnitude longer than the one explored in previous simulations [7,10], and allowed us to accurately quantify slow diffusional dynamics of H_2O molecules observed at the surface of tobermorite.

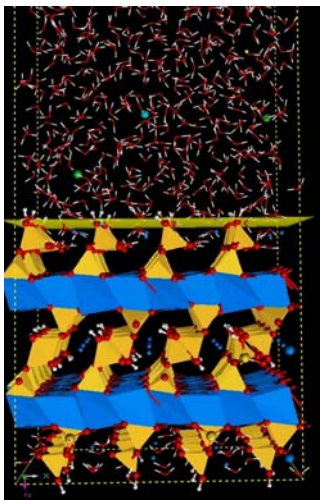

Fig. 1. The interfacial fragment of the MD simulation cell. The tobermorite structure is represented by distorted Ca-octahedra (blue), Si-tetrahedra (yellow), O (red balls), H (white balls). Water molecules are shown as red and white sticks, while the green and light blue balls represent Cl^- and K^+ ions, respectively.

Results and Discussion

If the location of the tobermorite-water interface is defined by the average positions of the exterior non-bridging oxygens of the bridging tetrahedra (yellow planes in Figs. 1 and 2a), it is possible to distinguish "internal" H_2O molecules that spend most of their time somewhat below the interface, within channels

between the tetrahedral chains on the tobermorite surface, from the "external" ones that reside above the interface. These two types of water molecules are clearly visible in the computed atomic density profiles shown in Figure 2.

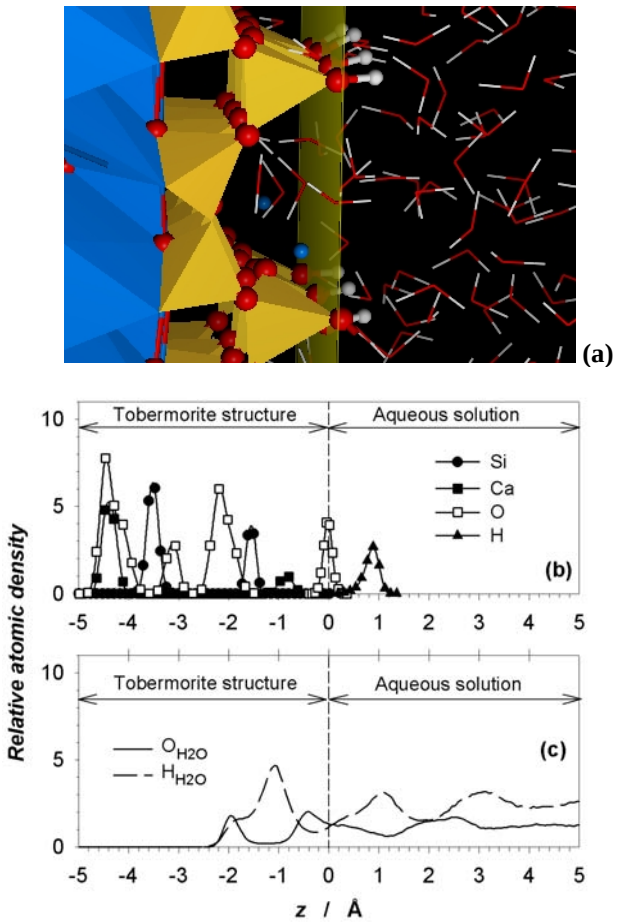

Fig. 2. Computed atomic density profiles for H_2O molecules (c), on the surface of 9Å tobermorite (a,b). The interface ($z = 0$) is nominally defined as the average position of the non-bridging oxygens (protonated; open squares) of the bridging silicate tetrahedra. The tobermorite substrate is located at negative z values, with Si of the bridging tetrahedra occuring at -1.6 Å (filled dots).The aqueous layer is generally located at positive z values, but some H_2O molecules can penetrate and remain as deep as -2.5Å below the interface into the tobermorite structrure.

Within the channels, there are two sub-layers of water molecules. One has its O_{H2O} atoms at about the level of the inner non-bridging oxygens (O_{NB}) of the bridging tetrahedra ($z \sim -2.0$ Å in Figure 2). The H_{H2O} shoulder at the same level is due to hydrogen bond donation from the water molecules to these Si-O^- sites. The second water sub-layer in the channels has its O_{H2O} about 0.4 Å below the level of the O_{SiOH}. The large H_{H2O} peak at about –1.2 Å is due to H-bond dona-

tion from these water molecules to the Si-O^-. There are three sub-layers of O_{H2O} at about 0.3, 1.8 and 2.6Å above the level of the O_{SiOH} that constitute the external surface-associated H_2O. The H_{SiOH} (the peak at ~0.9Å in Figure 2b) point outward and donate H-bonds to these $H_{H2O,}$ which in turn donate H-bonds to each other and to O_{SiOH}. Together, the O_{SiO-}, O_{SiOH}, H_{SiOH}, O_{H2O}, and H_{H2O} form a well-interconnected hydrogen bonding network within the channels and across the interface. The H_2O of the two layers in the channel and the closest layer outside the channels also complete the nearest neighbor coordination shell of the Ca ions of the surface (the peak at -0.85Å in Figure 2b). This surface-affected structuring of the H_{H2O} and O_{H2O} positions continues to at least 8Å above the interface [10].

As we have shown before [10], the "internal" water molecules within the channels ($-2.5 < z < 0$ Å in Figure 2c) donate H-bonds to both the bridging and non-bridging oxygens of the bridging Si-tetrahedra as well as to other H_2O. Some of these H-bonds can persist for as long as 100 ps, but many other "internal" water molecules can undergo libration (hindered rotations) and even diffusional jumps. The "external" H_2O molecules in the 3Å-thick layer above the nominal interface ($z = 0$ in Figure 2) are much more dynamically disordered by librational and diffusional motion than those in the channels.

The MD results yield diffusion coefficients of about $D = 5\times10^{-11}$ m^2s^{-1} for the "internal" water molecules that reside in the channels between the tetrahedral chains ($-2.5 < z < 0$ Å in Figure 2c) and about 6×10^{-10} m^2s^{-1} for the "external" water molecules that reside above them ($0 < z < 3$ Å in Figure 2c). These values are much less than the self-diffusion coefficient of bulk liquid water calculated for the same force field (of 2.3×10^{-9} m^2s^{-1}). At the same time, the T_1 relaxation rate values acquired from the recent field cycling relaxometry NMR measurements for OPC and other cement phases [1,2,15] indicate a mean residence time of a water molecule on the surface of approximately a few μs and a mean time between diffusional jumps on the surface of ~ 0.8-1.0 ns. The calculated diffusion coefficients of Ca^{2+} are somewhat less, 3.0×10^{-11} m^2/s in the channels and 5.0×10^{-11} m^2/s if they diffuse above the interface. For those K^+ and Cl^- associated with the surface, the diffusion coefficients (above the interface) are larger, 2.0×10^{-10} m^2/s and 3.8×10^{-10} m^2/s, respectively. No surface-bound Cl^- ions were observed on the timescale of our simulations. This result is in good agreement with the experimentally observed low Cl^- sorption capacity of this phase [17,24]. Cl^- sorption at similar sites on the actual C-S-H phase should be as low or even lower, because our tobermoite model contained a full set of Si-OH surface sites, whereas previous NMR studies have shown that at the Ca/Si ratios and pHs relevant to most cements the Si-O sites are deprotonated [25]. The negative charge of the bare surface O-atoms should repel the Cl^- even more strongly.

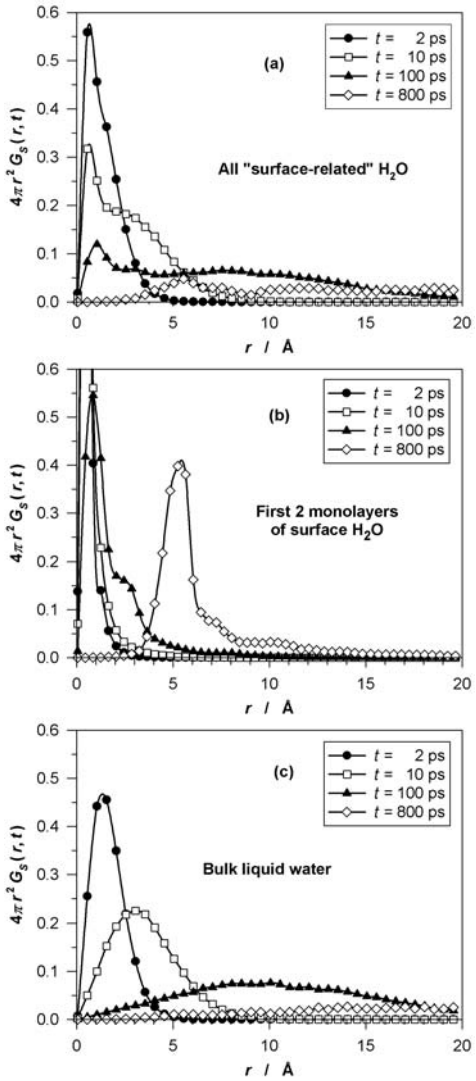

Fig. 3. *:* Van Hove self-correlation functions for diffusing H_2O molecules at the surface of tobermorite: (a) For all surface affected molecules; (b) for the first two surface H_2O monolayers only. The VHSCF behavior for bulk liquid water is shown in (c) for comparison.

Our present longer-time-scale MD simulations provide an opportunity to quantify these relatively slow diffusional motions of H_2O at the tobermorite interface by means of the Van Hove self-correlation function (VHSCF) [26],

$$G_S(r,t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \delta\left[r + r_i(0) - r_i(t)\right] \right\rangle, \qquad (1)$$

where r is the coordinate of the molecule, t is time, and N is the total number of molecules. This relationship describes the correlation in the positions of the same atom at different times, such that $4\pi r^2 G_S(r,t)\mathrm{d}r$ is the probability of finding an atom at distance r after a time t if the position of this atom was at the origin $r = 0$ at the initial time $t = 0$.

The Fourier transform of the VHSCF represents the incoherent or self-intermediate scattering function (SISF), which can be directly measured in incoherent quasielastic neutron scattering experiments and contains detailed information concerning the single-molecule dynamics both in time and space domain. The calculation of this correlation function for the water molecules strongly bound to the surface of tobermorite (within first two monolayers of H_2O at the surface) shows a dramatic difference in the dynamic behavior of adsorbed H_2O, as compared with the diffusional dynamics in bulk liquid water (Fig.3c), and yields a characteristic time scale of the diffusional process of the order of τ_m~0.8 ns (Figure 3b), in excellent agreement with NMR measurements, and points to a hopping diffusional mechanism with a length scale of l_m~5.5 Å, not unlike the characteristic lattice dimension of crystalline ice between two neighboring strong H-bonding sites.

From the 2-dimensional Einstein equation, $D = \langle|\mathbf{r}(t)- \mathbf{r}(0)|^2\rangle/4\tau$, the mean time for jumps between surface sites from the NMR results yield a diffusion coefficient of $0.9\times10^{-10}\ \mathrm{m^2 s^{-1}}$, which is also in remarkable agreement with the average diffusion coefficient for all surface-associated H_2O molecules obtained from MD simulations ($1.0\times10^{-10}\ \mathrm{m^2 s^{-1}}$). Here, $\mathbf{r}$ is the mean jump displacement (assumed to be 5.5 Å, from the results of the VHSCF calculations, Fig.3b) and τ is the mean jump time, $\tau \sim \tau_m \sim 0.8$ ns. This level of agreement definitely provides strong support for the interpretation of the experimental results.

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